Molecular-Scale Simulation of Clay Mineral Surface Geochemistry

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RESEARCH OBJECTIVES

This project involves basic research directed toward an accurate model of molecular structure at the surface of hydrated 2:1 clay minerals (smectites). These minerals, which are isostructural with micas (e.g., muscovite or biotite), are of great importance in petroleum production, nuclear waste containment, and contaminant attenuation by designed clay liners. The objective to be addressed is Monte Carlo (MC) and molecular dynamics (MD) simulations of interfacial molecular structure on smectite minerals adsorbing water and cations (counterions). The results obtained will provide a significantly improved quantitative understanding of clay–clay, clay–water, and cation–clay interactions that will be used to test existing experimental data and, if necessary, improve the potential function models used in the simulations.

APPROACH

Computational algorithms for the MC and MD simulations, based on the codes MONTE and MOLDY, have been developed by our collaborators, Dr. N. T. Skipper and Dr. K. Refson. These codes are fully optimized and running well on the Cray J90 and T3E supercomputers at the National Energy Research Scientific Computing Center (NERSC).

RESULTS

Monte Carlo and molecular dynamics (200 ps) simulations were performed to elucidate interlayer structure in hydrated lithium–hectorite (which is isostructural with biotite and has interlayer Li^+ counterions) at low water content ($H_2O/Li = 3$). Numerous spectroscopic studies of these stable clay mineral hydrates have led to an interlayer structural model based on a postulated inner-sphere surface complex comprising Li^+ bound directly to the hectorite surface while surmounted by exactly three solvating water molecules that execute hindered rotational motions around their symmetry axes (Figure 1). Our simulation results, based on tested water–water, Li^+–water, water–clay mineral, and Li^+–clay mineral potential functions, showed that outer-sphere surface complexes formed
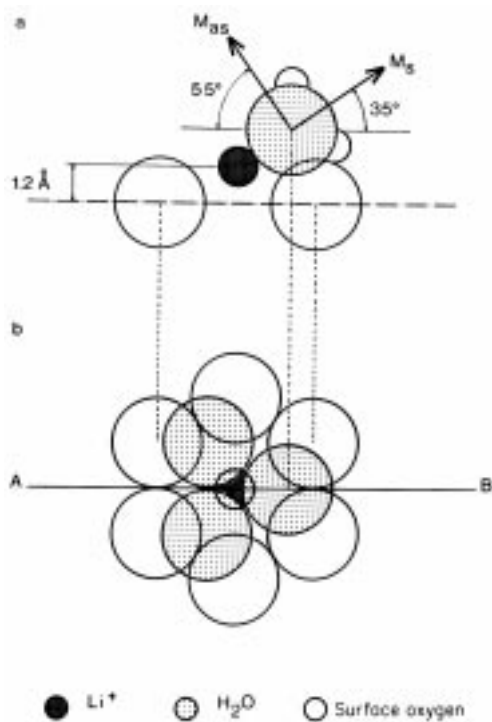

Figure 1. Spectroscopic model of a postulated trihydrate inner-sphere surface complex in $Li(H_2O)_3$–hectorite. Stipled circles denote water oxygens, open circles are hectorite surface oxygens, and the crosshatched circle is Li^+. The transition dipole moment vectors for IR-active symmetric and asymmetric stretching vibrations of the water molecule are denoted M_s and M_{as}, respectively. Upper view (a) is in the (z,x) plane and lower view (b) in the (y,x) plane. The angle of 35° between the dipole moment vector M_s and the horizontal line is confirmed by our MC simulations.

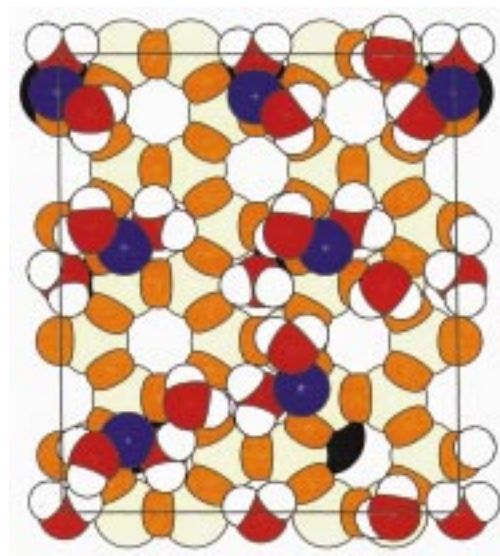Figure 2. Monte Carlo "snapshot" of the interlayer molecular configuration in $Li(H_2O)_3$-hectorite as seen in projection onto the (y,x) plane. Orange spheres denote surface oxygen ions; yellow spheres are structural Si^{4+} cations. Note that only two water molecules solvate each Li^+ (red O and white H), while the third (one is at the center of the figure) is keyed into a hexagonal cavity in the surface, evidently attracted to a hectorite structural proton (black sphere).
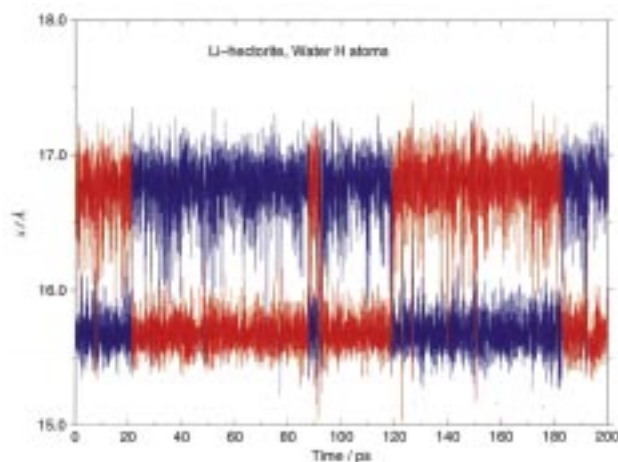
Figure 3. Molecular dynamics simulation of the time dependence of the *x*-coordinates (denoted in either red or blue) of a pair of protons in a water molecule that has keyed into a hexagonal cavity of the hectorite surface (see Figure 2). Note the sporadic exchange of *x*-coordinates, indicating that rotations of the H–H line of centers are occurring (on the picosecond time scale of the MD simulation).
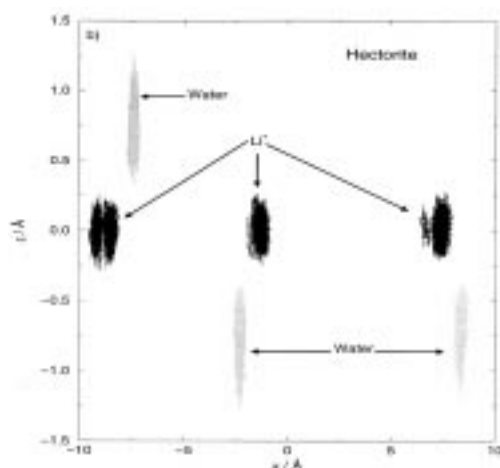

Figure 4. Molecular dynamics simulation of the cumulative trajectories (over 200 ps) of Li^+ (black) and three hydrating water molecules (gray) as seen in projection onto the (z,x) plane in the hectorite interlayer region. For reference, the oxygen ions in the hectorite surface are centered on the lines defined by $z = \pm1.88$ Å. This trajectory plot reveals vertical oscillatory motions of Li^+ (and its solvation shell) along an axis normal to the hectorite surface, in agreement with QNS spectral data. Lateral cation hopping between adjacent sites on the hectorite surface also is apparent.

instead on Li–hectorite, with water molecules interposed between Li^+ and the hectorite surface (Figure 2). The number of water molecules solvating each Li^+ in the clay hydrate was two, not three, and rotational motions of these water molecules did not occur. Instead, rotations around the symmetry axis occurred (Figure 3) only for water molecules attracted to protons inside the hexagonal cavities in the oxygen surface (Figure 2), thus strongly contradicting the spectroscopic model depicted in Figure 1.

Our MC simulation results for $Li(H_2O)_3$–hectorite were, however, in general agreement with the interpretation of both infrared (IR) and nuclear magnetic resonance (NMR) spectral data insofar as the average orientation of solvating water molecules is concerned (e.g., the 35° angle in Figure 1). Also, the Li^+ oscillations inferred from quasielastic neutron scattering (QNS) spectra were confirmed by our MD simulations (Figure 4).

SIGNIFICANCE OF FINDINGS

The MC and MD simulations indicated clearly that the inner-sphere trihydrate surface complex proposed for $Li(H_2O)_3$–hectorite on the basis of IR, QNS, and NMR spectroscopic data (Figure 1) was an oversimplification in several respects. First, outer-sphere surface complexes formed with the Li^+ solvation number are equal to two. Second, rotational motions in these surface complexes (at least over the 200-ps simulation time

scale) were absent. Water molecules in $Li(H_2O)_3$–hectorite that are not in surface complexes with Li^+ did show rotation around their symmetry axes, however (Figures 2 and 3). These major structural differences should be resolvable by developing new spectroscopic models guided by the results from this project and then comparing them with extant or new spectral data.

RELATED PUBLICATIONS

Greathouse, J., and G. Sposito, Monte Carlo and molecular dynamics studies of interlayer structure in $Li(H_2O)_3$–smectites, *J. Phys. Chem. B, 102*, 2406–2414, 1998,

Chang, F.-R.C., N. T. Skipper, and G. Sposito, Monte Carlo and molecular dynamics simulations of electrical double layer structure in potassium-montmorillonite hydrates, *Langmuir, 14*, 1201–1207, 1998.

FUNDING